

A Simple and Efficient SEC/GPC Linear Calibration Technique Using Broad-Range Standards

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SYNOPSIS

A simple method for calibrating high-performance SEC/GPC systems is presented. This technique sequentially finds the correct slope, D_2 , by tracking the calculated polydispersity, P , using arbitrary calibration slopes from which the intercept, D_1 , is ultimately back-calculated. The ease of application and relative efficiency of this search technique are highlighted and discussed. Theoretical justification of the simple form of the convergence equation is presented using two distribution models—the Gaussian (pseudo-Flory) and the sine (cosine) exponential models. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The development of high-performance size exclusion and gel permeation chromatography columns with stable and linear calibration characteristics has significantly extended the applicability and utility of the technique. These columns, when combined with modern HPLC pumps featuring excellent flow and metering capabilities, provide very rapid and precise measurement capabilities.¹ This forms the basis of a versatile tool for polymer analysis. Continued progress in SEC/GPC hardware development has produced a fair selection of relatively inexpensive devices for high-precision molecular weight analysis.^{2,3}

In spite of these advances, significant challenges remain concerning calibration of these systems. Calibration is required for the conversion of raw data (elution profiles) to molecular weight distribution (MWD) curves. The accuracy of results obtained from SEC elution data depends largely on the reliability of the calibration curve. Several calibration techniques have been reported,⁴⁻⁶ and several review articles⁷⁻¹⁰ discuss the more popular techniques in detail.

Choosing and implementing a calibration method depends on the availability of standards, hardware performance (e.g., band broadening), and software limitations. The two distinctly different approaches to calibration are called the peak-position method and the broad standard method. The peak-position method is easy to implement but requires the use of several narrow MWD polymer standards. In addition, to obtain high quality with this method, a secondary correction for band broadening is required. In contrast, the broad standard method uses only one or two broad MWD standards. However, this method requires significant amounts of computation and user expertise to obtain reliable results.

For a great number of situations, the most desirable technique would be one which enables the use of a single broad standard calibrant for a polymer system while avoiding extensive calculations and separate band broadening corrections. This method would also be relatively easy to implement and use.

We report here on a "broad standard" calibration technique developed for general-purpose SEC/GPC applications. It uses a single broad MWD standard sample, a linear SEC column set, and little else. The method can be used without recourse to dedicated programs or a computer. A hand-held calculator is quite sufficient to produce excellent results. This calibration method was first developed empirically, and then justified analytically. We describe the foundations and development of this method below.

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EMPIRICAL DEVELOPMENT

The strategy was to find functional relationships between the calibration coefficients and distribution characteristics using synthetic data. Combinations of sine and exponential decay functions were used to simulate data typically obtained from chromatographic experiments. Examples of these are shown in Figure 1. The moments of the MWDs were then calculated using the characteristic calibration curve intercept, D_1 , and curve slope D_2 . Figure 2 shows these parameters on a typical curve.

Inspection of the results revealed that the calculated polydispersity, P , was only a function of D_2 and independent of D_1 . This was in agreement with published results.¹¹ Further examination of the results revealed that for a series of values of D_2 on each simulated chromatogram, an equation could be written such that

$$\ln P = \ln S_1 + \ln S_2 D_2 \quad (1)$$

where S_1 and S_2 are parametric constants characteristic for each curve type. For two independent

determinations (subscripts a and b), it can easily be shown from eq. (1) that

$$S_2 = \frac{\ln(P_a/P_b)}{D_{2,a} - D_{2,b}} \quad (2)$$

The correct slope may thus be obtained from the same relationship by first assuming an arbitrary slope $D_{2,a}$, with a known slope S_2 , and resulting polydispersity, P_a . The final result is given simply by

$$D_{2,true} = \frac{\ln(P_a/P_{true})}{S_2} - D_{2,a} \quad (3)$$

An initial concern in implementing this technique was obtaining the value for S_2 . Extensive application has shown that very good results are obtained within four to five passes on a simple iteration for S_2 . Rapid convergence is quickly obtained over a wide range of values of S_2 and therefore, careful choice of S_2 is not critical.

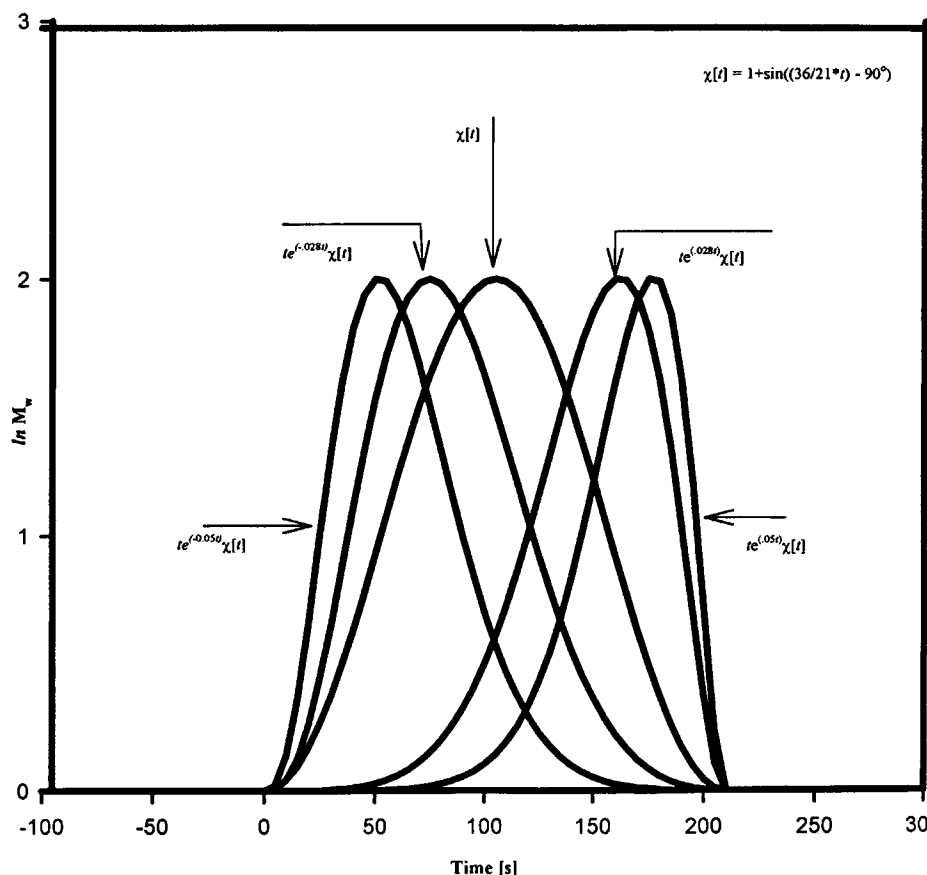


Figure 1 Synthetic distribution profiles.

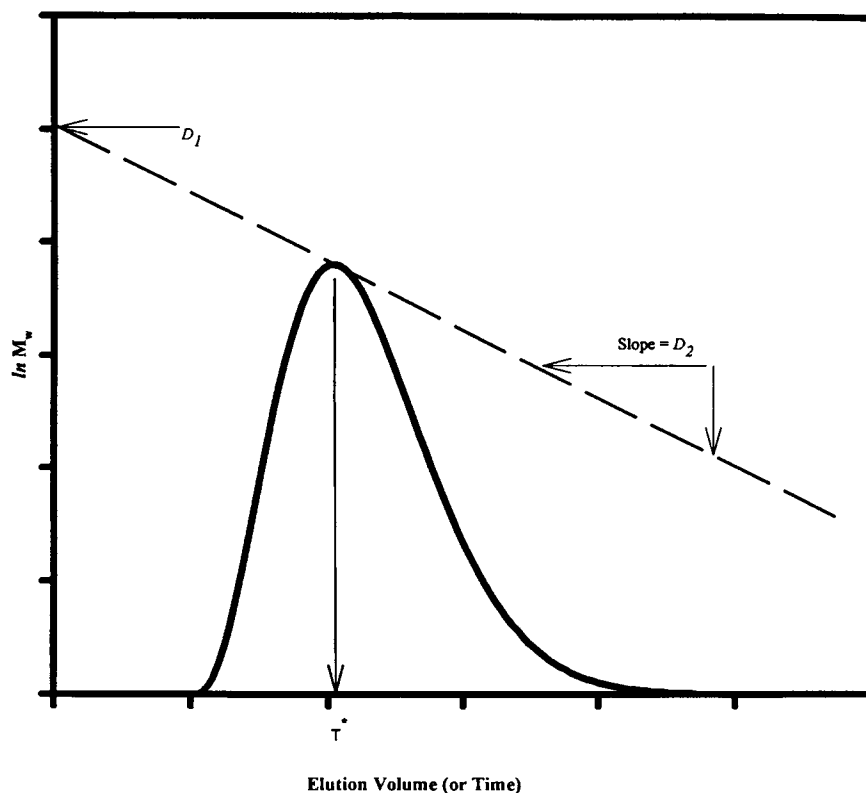


Figure 2 A typical calibration profile.

Once the “true value” of D_2 is obtained, the appropriate value of D_1 may be obtained from this new value and the two average molecular weight values, M_w . It can easily be shown from two independent determinations that

$$D_{1,\text{new}} = \ln M_{w,\text{new}} + (D_{2,\text{new}} T^*) \quad (4)$$

with

$$T^* = \ln(D_{1,\text{old}}/M_{w,\text{old}})/(D_{2,\text{old}}) \quad (5)$$

where T^* is the characteristic elution time for species with molecular weight equal to the average molecular weight.

In summary, the technique involves two steps: first rotation of the calibration curve to obtain the slope which produces the correct polydispersity (i.e., ratio of correct molecular weight values) and secondly, the translation of the calibration curve to produce the correct absolute value of the molecular weight numbers.

We have applied this technique to a wide variety of systems and obtained very good results. Sample data are included in Table I for a series of poly(vinyl chloride) (PVC) and polyethylene (PE) fractions. The results show excellent agreement between the

label values and the calculated results for the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the fractions. It is important to mention that in the data presented, convergence was achieved in no more than four iterations. The use of broad-range standards for this calibration makes this technique particularly attractive when combined with its ease of application.

This technique can also be very useful in reevaluating data generated from a different calibration curve. This is accomplished by using eqs. (3)–(5) with the “old data” and new calibration coefficients. We have applied this technique to a wide variety of systems and have obtained very good results. We present below a discussion of the theoretical basis of this technique.

ANALYTICAL JUSTIFICATION

The relative simplicity and general utility of this technique were rather surprising, and this prompted us to examine its analytical foundation. To this end, we examined the functional relationship between the calculated polydispersity and the calibration slope for a number of distributions. Even though a large

Table I Sample Analysis of Poly(Vinyl Chloride) (PVC) and Polyethylene (PE) Fractions for Number-Average (M_n) and Weight-Average (M_w) Molecular Weight

Sample	PVC I		PVC II		PVC III		PE	
	M_n	M_w	M_n	M_w	M_n	M_w	M_n	M_w
Label value	25,500	68,200	42,000	118,000	55,000	132,000	18,300	53,100
Analysis	28,100	75,100	44,500	116,000	54,700	139,300	18,000	52,800

number of possible distributions exists, we chose to examine those which are similar to most common chromatograms. The Gaussian (pseudo-Flory) and sine-exponential distributions are considered here.

Case I: The Gaussian (Pseudo-Flory) Distribution

For a log-normal MWD, the Flory most-probable distribution is closely approximated by the elution curve of a shape, Ξ , given by

$$\Xi = (2\pi)^{-1} \exp[(V - V_o)^2 / 2\sigma^2] \quad (6)$$

The polydispersity, P , can be written as the ratio of the weight-average to number-average molecular weights such that

$$P = \int_0^\infty \Xi \exp(-D_2 V) dV \times \int_0^\infty \Xi \exp(D_2 V) dV \quad (7)$$

V is the volume of a peak, V_o is the mean volume, and σ is a measure of the variance in the distribution. Close examination of the exponential terms under the integral signs shows that

$$[(V - V_o)^2 / 2\sigma^2] \pm D_2 V = [V - V_o \pm (D_2 \sigma^2)]^2 \quad (8)$$

Careful algebraic manipulation and subsequent integration gives the result

$$\ln P = [D_2 \sigma]^2 \quad (9)$$

For two independent determinations (subscripts i and j), it can easily be shown that

$$\ln(P_i/P_j) = \sigma^2[(D_{2i} + D_{2j})(D_{2i} - D_{2j})] \quad (10)$$

However, for most applications, $D_{2,i} \approx D_{2,j}$; for small changes in $D_{2,j}$ such that $D_{2,j} \gg \Delta D_{2,j}$, it follows, therefore, that the functional form

$$\ln(P/P_i) = \text{Const.}(D_2 - D_{2i}) \quad (11)$$

results. This is consistent with the results from our empirical observations.

Case II: The Sine-Exponential Distribution

For the offset sine (cosine) model, a similar approach may be adopted. In this case, the shape is given by

$$\Xi = \exp(aV) \cos(bV) \quad (12)$$

where a is the skew of the peak and b is the volume range of the peak. The polydispersity may be defined over a curve going from V_o to π/V . The resulting integral is given by

$$P = \left[\int_0^{\pi/b} \Xi \exp(-D_2 V) dV \times \int_0^{\pi/b} \Xi \exp(D_2 V) dV \right] / \left[\int_0^{\pi/b} \Xi dV \right]^2 \quad (13)$$

Defining α as the exponential decay factor, such that a can take on two values given by

$$a = \alpha \pm D_2 \quad (14)$$

and noting that

$$\int_0^{\pi/b} \Xi dV = \left[\sum_{n=0}^{\infty} \frac{a^{2n}}{b^{2n+1}} \right] \exp\left(\frac{a\pi}{b}\right) + \left[\sum_{n=1}^{\infty} (-1)^n \frac{a^{2n-1}}{b^{2n}} \right] \quad (15)$$

the polydispersity can be obtained to be

$$P = \frac{A + B}{C} \quad (16)$$

where,

$$A = (b^{-1}\exp(2\pi\alpha/b) - b^{-3}(\alpha - D_2))$$

$$[\exp(a + D_2) - \exp(a - D_2)] \quad (17)$$

$$B = \frac{a^2 - D_2^2}{b^4} \quad (18)$$

and

$$C = [b^{-1}\exp(a\pi/b)] - [\alpha/b^2]^2 \quad (19)$$

Values for the constants are $a \cong 0.028$, $b \cong 1.2$, and D_2 is typically of the order of -0.5 from which it can be shown that

$$B \approx 0 \quad (20)$$

Consequently, eq. (16) reduces to the functional form

$$P = \text{Const.}[\exp(D_2)] \quad (21)$$

which gives the expected result for two independent determinations,

$$\ln(P/P_o) = \text{Const.}(D_2 - D_{2o}) \quad (22)$$

In conclusion, it is important to point out that the analytical justification presented above is not unique to the two distribution functions discussed but is applicable to other models.

SUMMARY

A simple method for calibrating high-performance SEC/GPC systems is presented. This technique sequentially finds the correct slope, D_2 , by tracking

the calculated polydispersity, P , using arbitrary calibration slopes from which the intercept, D_1 , is ultimately back-calculated. The ease of application and relative efficiency of this search technique are highlighted and discussed. Theoretical justification of the simple form of the convergence equation is presented using two distribution models—the Gaussian (pseudo-Flory) and the sine (cosine) exponential models.

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